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Photooxidation of Allyl Chloride

Northrop Services, Inc.
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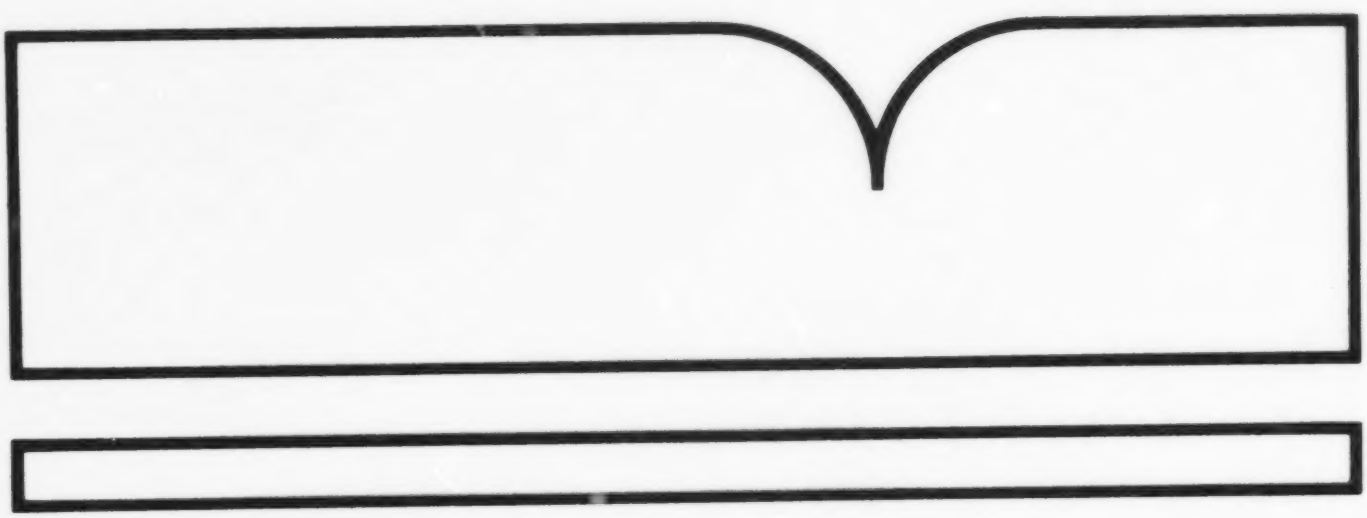

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16. ABSTRACT

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The Photooxidation of Allyl Chloride

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Abstract

The photooxidation of allyl chloride was studied by irradiation either in 100-L Teflon bags or in a 22.7-m^3 Teflon smog chamber in the presence of added NO_x. In the absence of added hydrocarbons, the reaction involves a Cl atom chain, which leads to a highly reactive system. A reaction mechanism is presented to account for the following photooxidation products: chloroacetaldehyde, formaldehyde, 1,3-dichloroacetone, 3-chloroacrolein, acrolein, glyoxal, chloroperoxyacetyl nitrate, and peroxypropenyl nitrate. The rate constant for OH reaction with allyl chloride at 298 K was measured by a relative rate method under conditions where the Cl atom chain length was small and was found to be $k_{OH} = 1.7 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}. The rate constant for O_3 reaction with allyl chloride at 298 K was found to be $k_{O_3} = 1.5 \times 10^{-18}$ cm^3 $molecule^{-1}$ s^{-1}.

Introduction

Allyl chloride (3-chloro-propene), a volatile industrial chemical, is present in urban atmospheres at the low parts per trillion level [1]. This fact is consistent with the relatively low level of allyl chloride emissions (500 tons/yr [1]) and its high reactivity to OH radicals. Allyl chloride is, however, a suspect carcinogen [1] and has been designated by EPA as one of 37 Hazardous Air Pollutants (HAPs) that are being considered for regulatory action. In order to assess the human health risks associated with exposure to atmospheric allyl chloride, it is necessary to determine its OH and O_3 reaction rate coefficients and the mechanisms by which it is converted to products. Neither the OH nor the O_3 reaction rate coefficients have been previously reported. The nature of the products generated from the photooxidation of HAPs is of considerable interest since many of the products may be toxic or mutagenic. For example, work in our laboratories indicates that chloroacetaldehyde, a major product of allyl chloride photooxidation, is a strong mutagen. We have also recently conducted experiments in which a bioassay of the total gas phase product mixture from allyl chloride photooxidation revealed a total mutagenic activity that was much greater than could be accounted for based on the concentration and mutagenic activity of chloroacetaldehyde.

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In this article, we report the results of several experiments aimed at obtaining accurate measurements of the rate constants for OH and O_3 reaction with allyl chloride and at determining the nature of the photooxidation products and the operative reaction mechanisms. The OH rate constant was obtained by using the relative rate method described by Atkinson [2] under conditions where the ratio of the reference compound (*n*-butane) to allyl chloride concentration was high and the Cl atom chain was unimportant. The O_3 rate constant was obtained by measurement of the O_3 decay under conditions that were pseudo first order with excess allyl chloride, according to the procedure described by Pitts et al. [3]. Product studies were conducted by irradiating mixtures of CH_3ONO, NO_x, and allyl chloride in ca. 100-L Teflon bags (CH_3ONO was used to generate OH radicals). Results from a smog chamber irradiation in which all identified reactants and products were measured as a function of time are reported. Based on the relative product formation rates in this experiment a detailed reaction mechanism is formulated to account for the production of the major products.

Experimental Procedures

Several preliminary product studies and the OH rate constant measurements were conducted in 100-L Teflon bags. The OH radicals were produced for these experiments by photolyzing methyl nitrite in the presence of NO, which generates OH as shown in reactions (1–3).

(1) $$CH_3ONO + h\nu \rightarrow CH_3O + NO$$

(2) $$CH_3O + O_2 \rightarrow HCHO + HO_2$$

(3) $$HO_2 + NO \rightarrow OH + NO_2$$

The methyl nitrite was prepared according to the procedure of Taylor et al. [4]. The light for the irradiations was supplied with a bank of five General Electric black lights. For these experiments, allyl chloride was measured with a Perkin Elmer 900 GC-FID, which contained a 3.2-mm inside diameter (i.d.) × 1-m long stainless steel column packed with Tenax GC, that was operated isothermally at 80°C. The *n*-butane was measured with a Gow-Mac 750 GC-FID which contained an identical column packed with Porapak QS that was operated isothermally at 150°C. Product identification for the CH_3ONO/NO_x/allyl chloride irradiations was conducted by cryogenically trapping (at 90 K) 5-L samples from the bags in a 20-cm^3 Pyrex sample loop. The contents of the sample loop were analyzed with an HP 5985 GC/MS that contained a 3.2-mm i.d. × 1-m long glass column paced with 1% SP-1000 on Carbopack B. The column temperature was programmed from 40°C to 200°C at 20°C/min. The MS was scanned from m/e = 34–200 at 0.4 s per spectrum during the GC/MS run.

The O_3 rate constant measurements were conducted with a 160-L Teflon bag, which was divided into two equal compartments with a partitioning clamp. Ozone for these measurements was produced by irradiating air that passed through a quartz tube with a low-pressure mercury lamp. Ozone was measured with a Bendix Model 8002 ozone analyzer.

The allyl chloride/NO_x irradiation was conducted in a 22.7-m^3 Teflon smog chamber. The chamber was constructed of a 7.5-m-long cylindrical Teflon bag connected on each end to 1.96-m diameter aluminum end plates, which were coated with fluorocarbon paint. Irradiation of the reactor was provided with a total of 180 GE F-40 blacklight bulbs and 36 sunlamps. Additional details of the reaction chamber have been published previously [5]. The NO and NO_x were measured for all experiments with a CSI Model 1600 oxides of nitrogen analyzer, which was calibrated with a certified standard of NO in N_2 obtained from MG Scientific. Ozone was measured with a Bendix Model 8002 ozone analyzer calibrated by using a Dasibi Environmental Corporation UV ozone monitor. For the smog chamber irradiation, allyl chloride was measured with an HP 5840 GC that contained a 3.2-mm i.d. glass column packed with 1% SP-1000 on Carbopack B and was operated isothermally at 75°C. Detection for this GC was conducted with an HNu Systems Inc. photoionization detector. Samples for determination of chloroaceteldehyde, 3-chloroacrolein, and 1,3-dichloroacetone were obtained by bubbling 10-L chamber samples through 2 cm^3 of methanol cooled to 0°C in an impinger bottle. Collection efficiency for this technique was found to be ≥99%, as determined by using two bubblers in series. These three compounds were separated by using the same column used in the HP5840 GC in a Varian 1200 GC with a Valco Model 140B electron capture detector. Chloroacetaldehyde and 1,3-dichloroacetone were identified from their chromatographic retention times (using pure commercial samples), and from their mass spectra. The 3-chloroacrolein was identified from its mass spectrum only, since a standard could not be obtained (see Results and Discussion section). The electron capture detector sensitivity for 3-chloroacrolein was assumed to be identical to that for chloroacetaldehyde. Formaldehyde, acrolein, and glyoxal were identified and measured by using a dinitrophenylhydrazine/high performance liquid chromatography (DNPH/HPLC) technique [6]. The reacted hydrazones were separated in a column packed with Zorbax ODS and detected by using a Varian Model 5000 HPLC equipped with a UV/VIS absorption detector and operated at 360 nm. Calibrations were performed by using dilute solutions of twice-recrystalized hydrazone samples for each aldehyde.

Peroxypropenyl nitrate (A-PAN) and chloro-peroxyacetyl nitrate (C-PAN) were measured with a Varian electron capture detector after separation on a column packed with 10% Carbowax 400 on 80/100

Supelcoport at 25°C. Retention times were determined by injecting a sample from an irradiated mixture of Cl_2, NO_2, and the appropriate aldehyde (acrolein and chloroacetaldehyde, respectively) in air. The A-PAN and C-PAN calibrations were performed by assuming that the change in aldehyde concentration after irradiation of the appropriate aldehyde/Cl_2/NO_2/air mixture was equal to the final A-PAN or C-PAN concentration. Results from our laboratory with peroxyacetyl nitrate indicate that for stoichiometric mixtures that are not photolyzed to completion, this was a reasonably good assumption.

Results and Discussion

$C_3H_5Cl/CH_3ONO/n-C_4H_{10}/NO_x$ Irradiation

The rate constant for OH reaction with allyl chloride can be determined by a relative rate method if CH_3ONO is photolyzed in the presence of allyl chloride and a reference organic for which the OH rate constant is known. We chose *n*-butane since the rate constant is well known [2], and the relative decay rates for allyl chloride and *n*-butane would be similar at reasonably high $[n-C_4H_{10}]/[C_3H_5Cl]$ ratios. The *n*-butane also serves as an effective scavenger for Cl atoms. In this study, 15 irradiations were conducted, all with allyl chloride concentrations of 4.0 ppm and with *n*-butane concentrations ranging from 1.0 to 64.0 ppm. Allyl chloride and *n*-butane concentrations were measured by GC as a function of time during the irradiations. If reactions (4) and (5) dominate the hydrocarbon removal process, then eq. (I) will yield k_4/k_5 via plots of $\ln([C_3H_5Cl]_0/[C_3H_5Cl]_t)$ vs. $\ln([n-C_4H_{10}]_0/[n-C_4H_{10}]_t)$.

(4) $$OH + C_3H_5Cl \rightarrow \text{Products} + \alpha Cl$$

(5) $$OH + n-C_4H_{10} \rightarrow \text{Products}$$

(I) $$\ln\left(\frac{[C_3H_5Cl]_0}{[C_3H_5Cl]_t}\right) = \frac{k_4}{k_5}\ln\left(\frac{[n-C_4H_{10}]_0}{[n-C_4H_{10}]_t}\right)$$

This analysis becomes complicated since, it would appear from the product analysis, Cl atoms are produced some fraction (α) of the time for reaction (4). If for reactions (6) and (7), k_6/k_7 is sufficiently different from k_4/k_5, the slope of the plot calculated with eq. (1) will be a function of $[n-C_4H_{10}]_0/[C_3H_5Cl]_0$, since reaction (7) removes Cl atoms. That is, as this ratio increases, the Cl atom concentration will decrease.

(6) $$Cl + C_3H_5Cl \rightarrow \text{Products} + \beta Cl$$

(7) $$Cl + n-C_4H_{10} \rightarrow \text{Products}$$

A plot of the observed k_4 vs. $[n-C_4H_{10}]_0/[C_3H_5Cl]_0$ is presented in Figure 1, where $[C_3H_5Cl]_0 = 4.0$ ppm for all data and the error bars

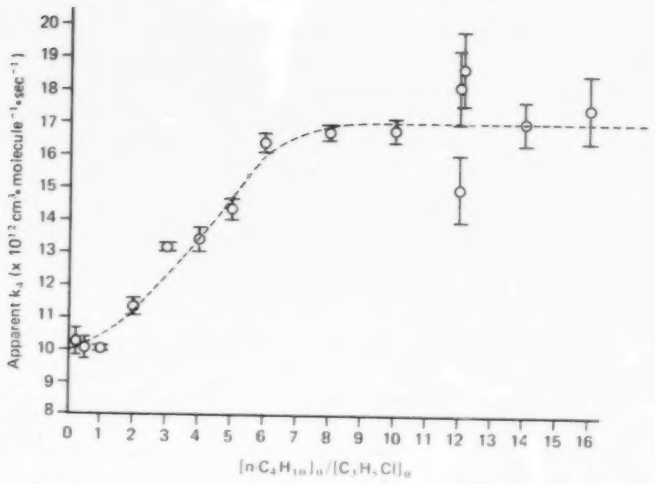


Figure 1. Apparent k_4 as a function of reactant concentrations.

represent plus or minus two standard errors in the slope. The k_4 values are calculated using the value $k_5 = 2.53 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} [2]. As can be seen from Figure 1, the apparent k_4 (or k_4/k_5) increases as $[n\text{—}C_4H_{10}]_0/[C_3H_5Cl]_0$ increases, but levels off beyond $[n\text{—}C_4H_{10}]_0/[C_3H_5Cl]_0 \geq 5$. If one assumes that as $[n\text{—}C_4H_{10}]/[C_3H_5Cl]_0$ increases [Cl] decreases, the necessary condition for this effect is that $k_4/k_5 > k_6/k_7$. Although we have no information regarding the value for k_6, the analogous values for k_4/k_5 and k_6/k_7 for propylene and n-butane (i.e., taking propylene as a model for allyl chloride) are 10.4 and 1.4, respectively (unpublished data from our laboratories). If we assume that for $[n\text{—}C_4H_{10}]_0/[C_3H_5Cl]_0 \geq 5$ the relative importance of reactions (6) and (7) is small [compared with reactions (4) and (5)], the data in Figure 1 lead to our best estimate of $k_4 = 1.70\ (\pm 0.34) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. (The indicated uncertainty is $\pm 3\sigma$ using the data where $[n\text{—}C_4H_{10}]_0/[C_3H_5Cl]_0 > 5$.)

A steady state assumption for Cl atoms applied to reactions (4) through (7) yields the following expression for the ratio [Cl]/[OH], where $\gamma = (1 - \beta)$, $[R] = [n\text{—}C_4H_{10}]$ and $[T]$ = [allyl chloride]:

$$\text{(II)} \qquad \frac{[\text{Cl}]}{[\text{OH}]} \simeq \frac{\alpha k_4}{k_7[R]/[T] + \gamma k_6}$$

Using this equation, we can calculate [Cl]/[OH] for $[R]/[T] = 5$, assuming the value $k_4 = 1.70 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} is correct. As a worst case scenario, we will assume that $\alpha = 0.6$, since the yield of chloroacetaldehyde is ca. 40% (see discussion below), and that $\gamma = 0$

(i.e., $\beta = 1$). The latter is clearly an underestimation of γ since it would appear that the production of 1,3-dichloroacetone represents a termination step for Cl. Using the value for k_7 of 2.2×10^{-10} cm^3 molecule^{-1} s^{-1} [7] leads to [Cl]/[OH] = 9×10^{-3} at $[R]/[T] = 5$. The relative importance of reaction (6) versus reaction (4) can then be calculated as $R_6/R_4 = (k_6/k_4) \cdot 9 \times 10^{-3}$ and reactions (7) vs. (5) as $R_7/R_5 = (k_7/k_5) \cdot 9 \times 10^{-3}$. Assuming that k_6 is the same as that for Cl reaction with propylene ($k(\mathrm{Cl} + \mathrm{C_3H_6}) = 2.24 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} [8]) leads to $R_6/R_4 = 0.12$, or 11% of the removal rate for allyl chloride. Using the values $k_5 = 2.53 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} [2] and $k_7 = 2.2 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} leads to $R_7/R_5 = 0.78$, or 44% of the removal rate for *n*-butane. If this analysis is correct, it would indicate a significant underestimation of k_4 at $[R]/[T] = 5$. It is possible that this reflects, in part, an unrealistically high value for α. The value for α can, however, be estimated if we assume that at high $[R]/[T]$, the rate of reaction (6) is negligibly small relative to that of reaction (7). This is probably reasonable given the magnitude of k_7. In this case, the second term in the denominator of expression (II) is removed, and under these conditions α can then be calculated from a plot of $\ln([R]_0/[R_t])/\ln([T]_0/[T]_t)$ versus $[T]_0/[R]_0$, as indicated in expression (III), which results from combining and integrating the rate expressions for R and T and substitution of expression (II).

$$\text{(III)} \qquad \frac{\ln([R]_0/[R]_t)}{\ln([T]_0/[T]_t)} = \alpha\frac{[T]_0}{[R]_0} + \frac{k_5}{k_4}$$

This analysis leads to an estimated value $\alpha = 0.20 \pm 0.08$. This seems to be a very reasonable estimate since, in the allyl chloride/NO_x irradiation, the initial yield of 1,3-dichloroacetone (the principal fate of Cl atom reaction with allyl chloride) is ca. 15% (see Figs. 4 and 5). This value of α then leads to [Cl]/[OH] = 3×10^{-3}, $R_6/R_4 = 0.04$, and $R_7/R_5 = 0.26$ at $[R]/[T] = 5$. At the highest ratio of $[R]/[T] = 16$, R_7/R_5 becomes 0.08, or 8% of the total *n*-butane removal rate. This analysis therefore indicates that the asymptotic value of $k_4 = 1.7 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} obtained from Figure 1 probably does not contain a significant contribution from Cl atom reaction, and is therefore a good estimate. The fact that the curve becomes flat at $[R]/[T] > 5$ is a good indication that Cl atoms are effectively scavenged by $n\text{—}\mathrm{C_4H_{10}}$. However, given the inexact nature of this treatment, a more reasonable experimental uncertainty for k_4 is ±40%, or $k_4 = 1.7(\pm 0.7) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}.

The fact that OH reaction with allyl chloride yields Cl atoms a fraction of the time was evidenced from the preliminary GC/MS analysis of the irradiated $\mathrm{C_3H_5Cl/CH_3ONO/NO_x}$/air mixtures. A relatively major product, 1,3-dichloroacetone, was identified on the basis of its GC retention time and its published electron impact (EI) mass spectrum

[9]. This compound most likely would be produced as a result of Cl atom addition to the double bond of allyl chloride. The presence of a relatively minor product, acrolein, which was identified based on the HPLC retention time of its DNPH hydrazone, also indicates the production of free Cl atoms. Two other products identified by GC/MS were chloroacetaldehyde and 3-chloroacrolein. Although the former was identified on the basis of its GC retention time and its published mass spectrum [9], neither an authentic sample of 3-chloroacrolein nor a published mass spectrum was available. The mass spectrum that we obtained for the product identified as 3-chloroacrolein is presented in Figure 2. Two other products identified with the DNPH technique were formaldehyde and glyoxal, the former being a major product.

O_3 Rate Constant Determination

The ozone rate constant was determined by filling one side of the 100-L Teflon bag with ca. 0.4-1 ppm O_3, and the other side with ca. 10 times that quantity of allyl chloride. When the O_3 concentration stabilized, the clamp dividing the bag was removed, and the reactants were allowed to mix (ca. 1 min). The O_3 decay was then monitored for ca. 90 min. The O_3 decay represents the sum of the rates for reactions (8) and (9) below.

$$O_3 + C_3H_5Cl \rightarrow \text{Products} \tag{8}$$

$$O_3 \xrightarrow{\text{wall}} \text{(Removal)} \tag{9}$$

This mechanism leads to the rate expression $\ln[O_3]_0/[O_3]_t = k' \cdot t$, where for pseudo first-order conditions, $k' = k_8[C_3H_5Cl] + k_9$. Values for k_8 can therefore be obtained from the slope of the plots of $\ln[O_3]_0/[O_3]_t$ vs. t, since the values for k_9 and $[C_3H_5Cl]$ are known. Three experiments were conducted in which k_9 was measured in a separate experiment before the k' was measured. The results are presented in Table I, which includes values for the correlation coefficient, r, from the

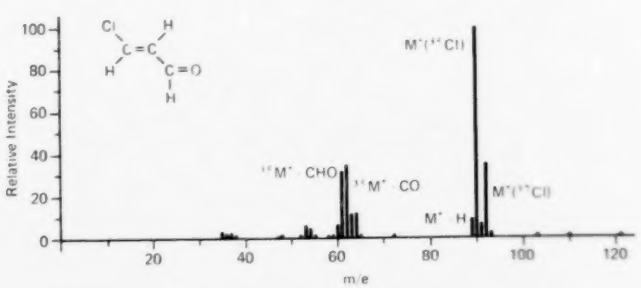


Figure 2. Mass spectrum of 3-chloroacrolein.

TABLE I. Reaction concentration and results for k_{O_3} determination.

$[O_3]_0$, ppm	$[C_3H_5Cl]_0$, ppm	r	k_8, s^{-1}	k_8, cm^3-molecule^{-1}-s^{-1}
0.173	2.0	0.99939	1.5×10^{-5}	1.48×10^{-18}
0.474	10.0	0.99995	1.3×10^{-5}	1.50×10^{-18}
0.457	10.0	0.99995	1.3×10^{-5}	1.54×10^{-18}

three plots. As an example, a plot of the data for the 10.0-ppm allyl chloride/0.474-ppm O_3 experiment is presented in Figure 3. It is clear from these data that the results are reproducible and that the plots are linear. However, a possible complication is the question as to whether O_3 reaction with allyl chloride yields free Cl atoms. If this were the case, the data in Table I would be regarded as upper limits since the apparent O_3 decay rate would be faster due to Cl atom reaction with O_3. However, the linearity of the plots and the fact that the k_8 determinations were independent of the reactant concentrations tends to argue against this possibility. Since Cl atom reaction with allyl chloride undoubtedly yields additional Cl atoms, the apparent k_8 would be dependent on the ratio $[C_3H_5Cl]/[O_3]$, which does not appear to be the case. In addition, since allyl chloride is in excess, the Cl atoms would be effectively scavenged by allyl chloride (k_6 is fast), which would impact on the k_8 measurement only if [allyl chloride] was significantly depleted. In that case there would be curvature in the plots, which, again, was not observed. We recommend an average value for k_8 of 1.5×10^{-18} cm^3 $molecule^{-1}$ s^{-1} (The uncertainty of the measurements is ca. ±15%.).

The rate constant data for OH and O_3 reaction with allyl chloride obtained here allow us to calculate the atmospheric lifetimes (τ_{OH} and

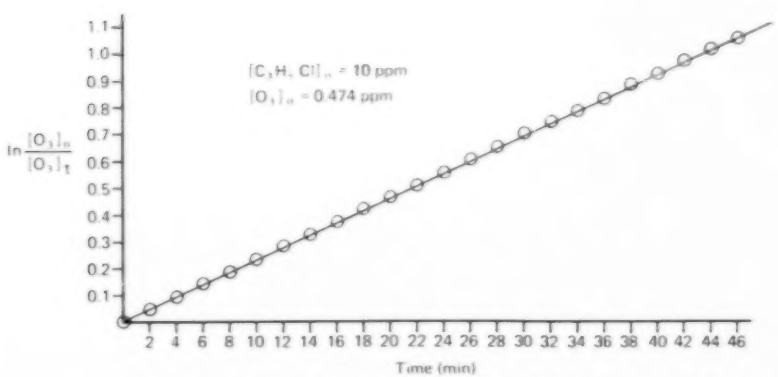


Figure 3. Sample plot for k_8 determination.

τ_{O_3}) for allyl chloride reaction with those species. Using as typical daytime OH and O_3 concentrations, 2×10^6 and 2×10^{12} molecules/cm^3, respectively, we obtained $\tau_{OH} = (k_4\ 2 \times 10^6\ \text{molecules/cm}^3)^{-1} = 8.2$ h, and $\tau_{O_3} = (k_8\ 2 \times 10^{12}\ \text{molecules/cm}^3)^{-1} = 92$ h. It is clear from these data, therefore, that the dominant atmospheric removal mechanism for allyl chloride is reaction with OH.

C_3H_5Cl/NO_x Irradiation

Once we had identified the major products, we conducted an allyl chloride/NO_x irradiation in a 22.7-m^3 Teflon smog chamber in order to obtain time profiles for the various reactants and products. Reactants and products measured during this experiment were allyl chloride, NO, NO_x, O_3, chloroacetaldehyde, formaldehyde, 1,3-dichloroacetone, 3-chloroacrolein, glyoxal, acrolein, C-PAN, and A-PAN. The latter two were secondary products that resulted from the oxidation of chloroacetaldehyde and acrolein, respectively. The concentration-time profiles for these species are presented in Figures 4 and 5.

It is clear from examination of Figure 5 that chloroacetaldehyde and formaldehyde are major products. By analogy with acetaldehyde and formaldehyde production from propylene photooxidation [10], it would seem reasonable that the predominant routes for chloroacetaldehyde and formaldehyde production are as shown in reactions (10) through (13) below.

Alternatively, the OH radical can abstract from the carbon-3 position to yield the resonance-stabilized allyl radical, as shown in reactions (14) and (15).

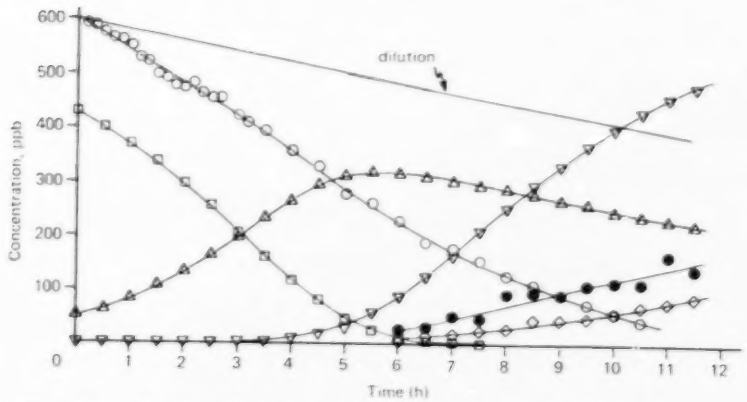


Figure 4. Allyl chloride/NO_x irradiation; reactants profile. ○ Allyl chloride, □ NO, △ NO_x-NO, ▽ O_3, ● C-PAN, ◇ A-PAN × 5.

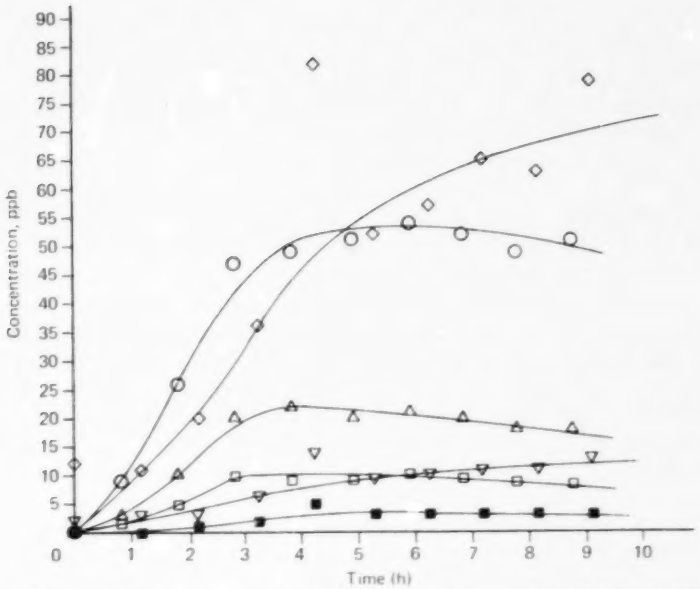
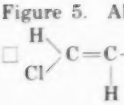


Figure 5. Allyl chloride/NO, irradiation; products profile. ○ CH_2ClCHO, □  △ 1,3-dichloroacetone, ◇ HCHO, ▽ Glyoxal, ■ Acrolein.

(14) $OH\ (or\ Cl) + C_3H_5Cl \longrightarrow \cdot CHClCH = CH_2 + H_2O\ (or\ HCl)$

(15,-15) $\cdot CHClCH = CH_2 \rightleftharpoons CHCl = CHCH_2\cdot$

We can then account for formation of acrolein and 3-chloroacrolein in reactions (16) through (19).

(10) $OH + C_3H_5Cl \xrightarrow{O_2,NO} CH_2ClCH(O)CH_2OH + NO_2$

(11) $OH + C_3H_5Cl \xrightarrow{O_2,NO} CH_2ClCH(OH)CH_2O + NO_2$

(12) $CH_2ClCH(O)CH_2OH \xrightarrow{O_2} CH_2ClCHO + HCHO + HO_2$

(13) $CH_2ClCH(OH)CH_2O \xrightarrow{O_2} CH_2ClCHO + HCHO + HO_2$

(16) $\cdot CHClCH = CH_2 + O_2 \xrightarrow{NO} CHCl(O)CH = CH_2 + NO_2$

(17) $CHCl = CHCH_2 + O_2 \xrightarrow{NO} CHCl = CHCH_2O + NO_2$

(18) $CHCl(O)CH = CH_2 \longrightarrow CH_2 = CHCHO + Cl$

(19) $CHCl = CHCH_2O + O_2 \longrightarrow CHCl = CHCHO + HO_2$

The Cl atom produced in reaction (18) can then add to the double bond of allyl chloride to produce 1,3-dichloroacetone, as shown in reactions (20) and (21).

(20) $Cl + C_3H_5Cl \xrightarrow{O_2,NO} CH_2ClCH(O)CH_2Cl + NO_2$

(21) $CH_2ClCH(O)CH_2Cl + O_2 \longrightarrow CH_2ClC(O)CH_2Cl + HO_2$

However, it is clear from Figure 5 that the 1,3-dichloroacetone yields are significantly greater than the sum of the acrolein plus glyoxal yields (glyoxal is an acrolein photooxidation product), and therefore reaction (18) is clearly not the only source of Cl atoms. Given the fact that 1,3-dichloroacetone is produced in significant yields and is produced in a Cl atom chain-terminating step, it would seem reasonable that some of the Cl atoms are produced in a step along with HO_2 radicals, which will propagate the chain after reaction with NO to produce OH. It is not obvious to us what the actual source is, however. Since the three chlorine-containing products account for roughly 60% of the reacted allyl chloride, it is possible that there are products involved in the Cl atom chain that we have not identified.

The glyoxal is produced from OH reaction with acrolein, as shown below.

(22) $OH + CHOCH = CH_2 \xrightarrow{O_2,NO} CHOCH(O)CH_2OH + NO_2$

(23) $CHOCH(O)CH_2OH \xrightarrow{O_2} (CHO)_2 + HCHO + HO_2$

C-PAN and A-PAN are produced from OH reaction with a chloroacetaldehyde and acrolein respectively, as indicated in reactions (24) and (25).

(24) $OH + CH_2ClCHO \xrightarrow{O_2,NO_2} CH_2ClC(O)OONO_2 + H_2O$

(25) $OH + CH_2 = CHCHO \xrightarrow{O_2,NO_2} CH_2 = CHC(O)OONO_2 + H_2O$

Since the glyoxal, A-PAN, and C-PAN are secondary products, they should be produced with a slight induction period, as indicated in Figures 4 and 5.

Conclusions

It is apparent from this study that the photooxidation of allyl chloride can occur at least in part through a Cl atom chain reaction, which markedly affects the apparent photochemical reactivity of allyl chloride/NO_x mixtures. Our relative rate study resulted in a rate constant for OH reaction with allyl chloride of $1.7(\pm 0.34) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K. We also measured the rate constant for O_3 reaction with allyl chloride and found $k_{O_3} = 1.5 \times 10^{-18}$ cm^3

molecule^{-1} s^{-1}. The dominant atmospheric removal process for allyl chloride is by reaction with OH. Although chloroacetaldehyde and formaldehyde were found, as expected, to be major products, 1,3-dichloroacetone was produced in significant quantities as a result of Cl atom reaction with allyl chloride. It should therefore be noted that any reactivity studies or rate constant measurements with allyl chloride as a reactant should take into account the contribution of Cl atoms to the reaction rate.

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